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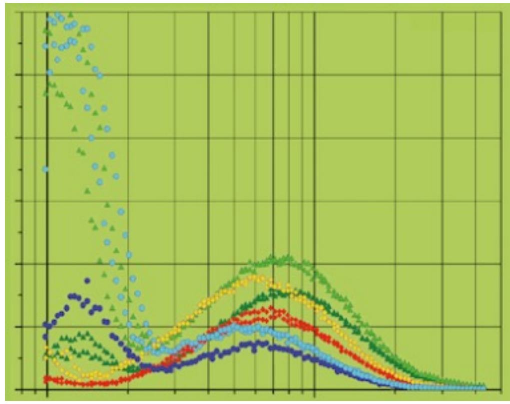

25th ETH-Conference on Combustion Generated Nanoparticles

June 21-23, 2022, Online Conference

Flame, Aerosol, and Nano Technologies Laboratory (FANTastic Lab)

flamenanoaerosol.wordpress.com

In-situ Characterization of Catalyst Nanoparticles from Reactive Spray Deposition Technology (RSDT)

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University of Connecticut

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Reactive Spray Deposition Technology (RSDT)

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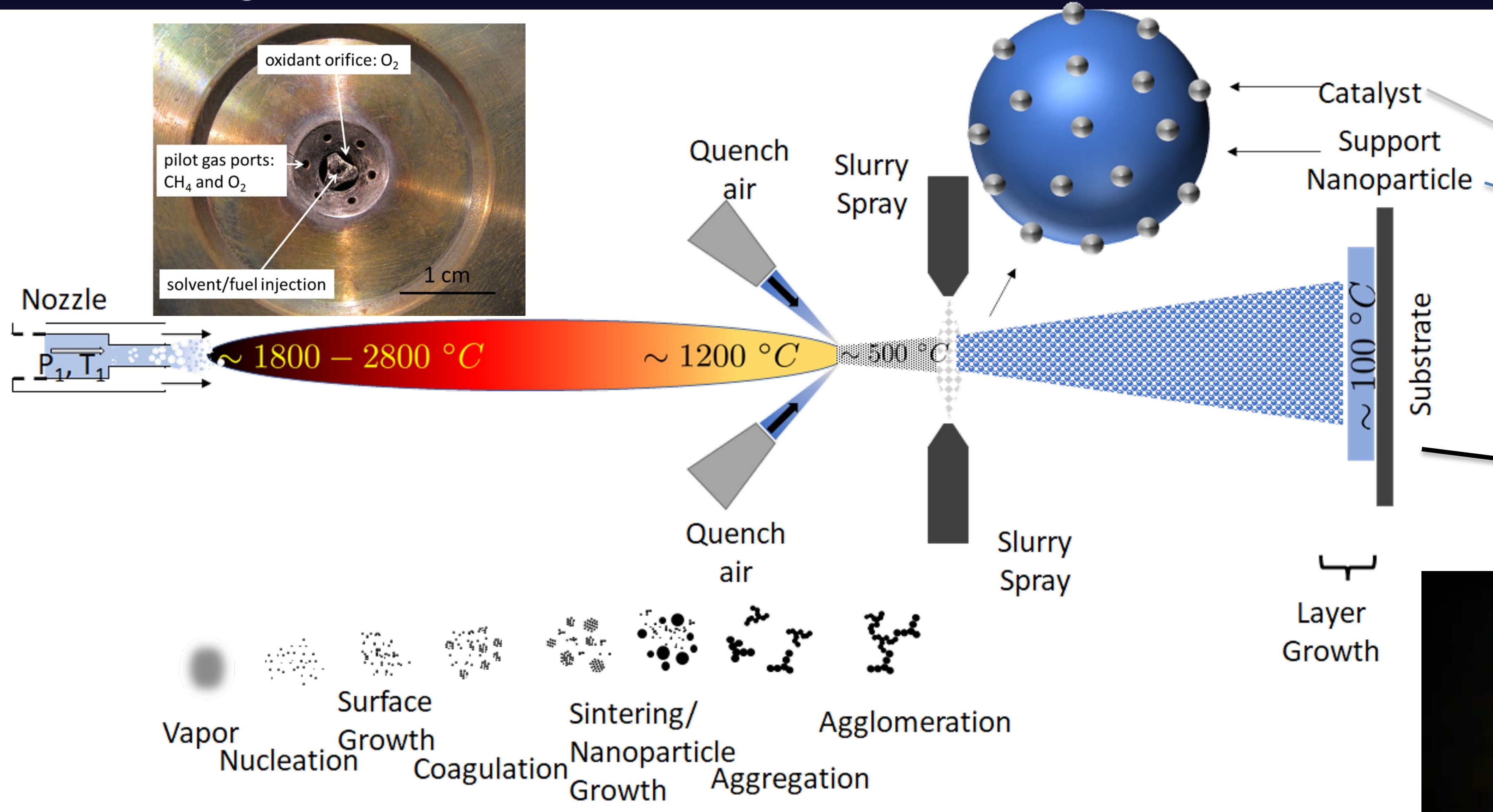
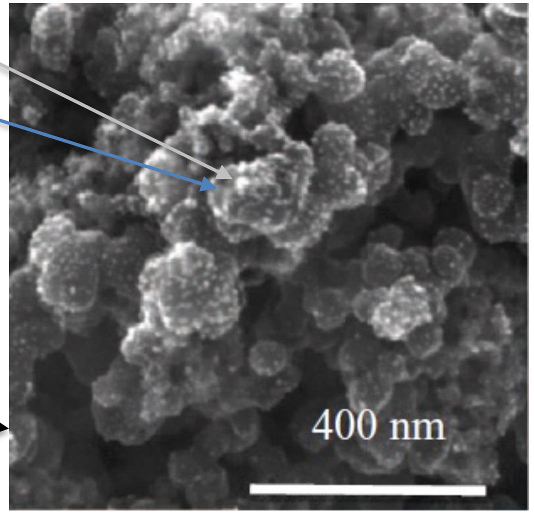
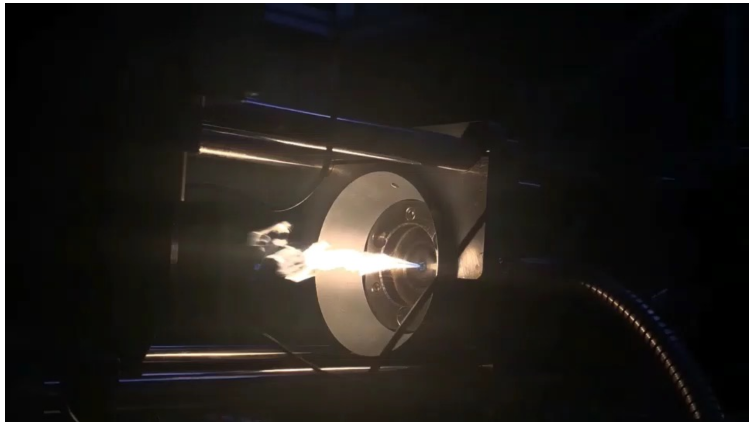
RSDT Diagram







One-step flame-based process which is used in fuel cell, electrolyzer, and battery catalyst layer manufacturing

- ❑ **Synthesized nanoparticles < 10nm**
- ❑ **Process optimization could be accelerated by in-situ measurements (e.g. particle size distribution, number concentration)**

Yu et al., 2014, *J. Electrochem. Soc.*, *161*, F622
Roller et al.,2013, Electrochim. Acta, 107, 632-655

RSDT Setups

Flames under investigation

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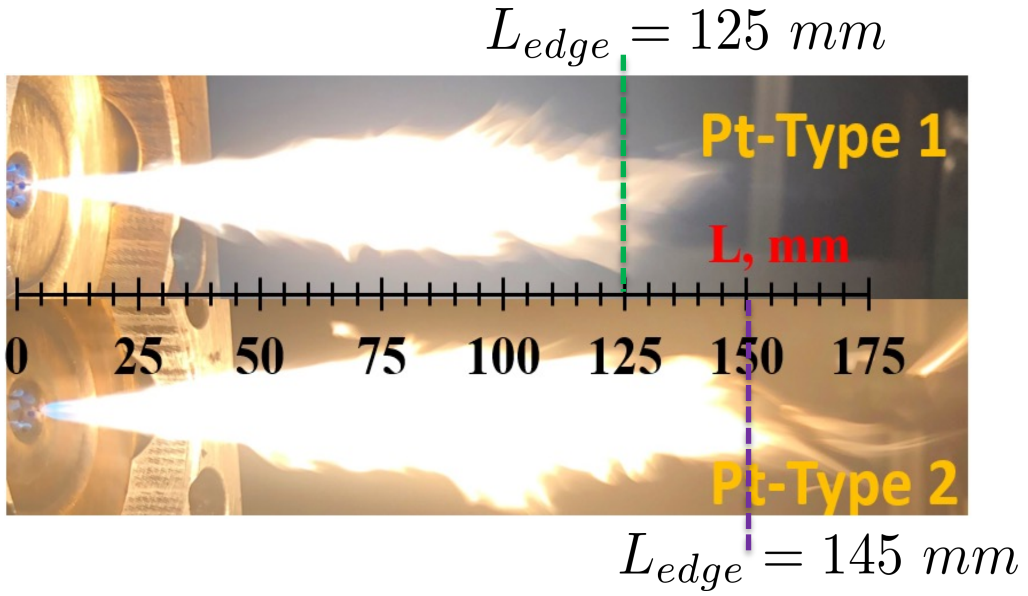
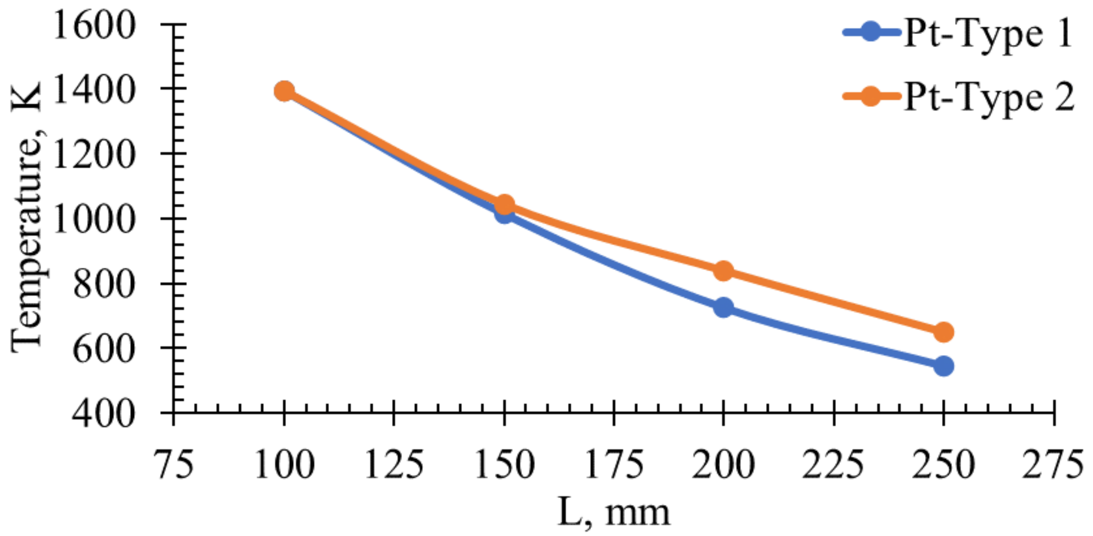
- Two pairs of flames with different liquid fuel flowrates
- The two flames of the pairs differ only on the presence and the absence of the precursor (PtAcAc) in the solution
- The average image of the flame is utilized to measure the flame length



Solvents in liquid fuel: acetone, xylene, liquid propane

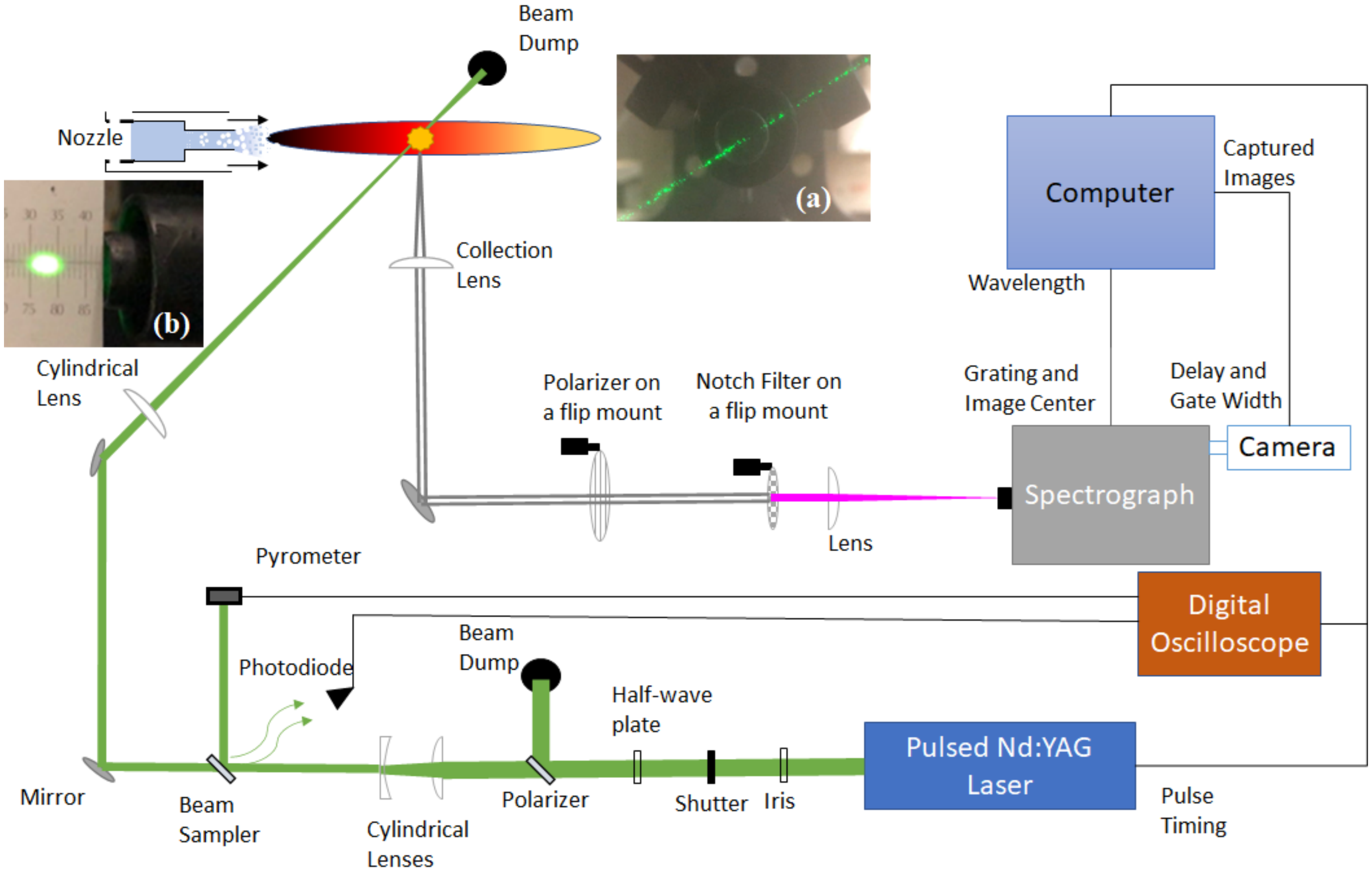
Precursor: Platinum Acetylacetonate (PtAcAc)

Flame name	Liquid fuel mixture (mL/min)	O_2 (SLPM)	Pilot CH_4 flow rate (SLPM)	Pilot O_2 flow rate (SLPM)	PtAcAc in liquid fuel
Pt-Type 1	4	7.3	0.55	0.55	10 mM
Pt-Blank 1	4	7.3	0.55	0.55	-
Pt-Type 2	7	11	0.75	0.75	10mM
Pt-Blank 2	7	11	0.75	0.75	-



- **Light Scattering (LS)**
  - Gate time 20 ns
  - Polarizer installed
  - No Notch filter

- **Laser Induced Incandescence (LII)**
  - Gate time
    - 150 ns
    - 250 ns
    - 350 ns
  - No polarizer
  - Notch filter installed



Static Scattering

Scattering Coefficient

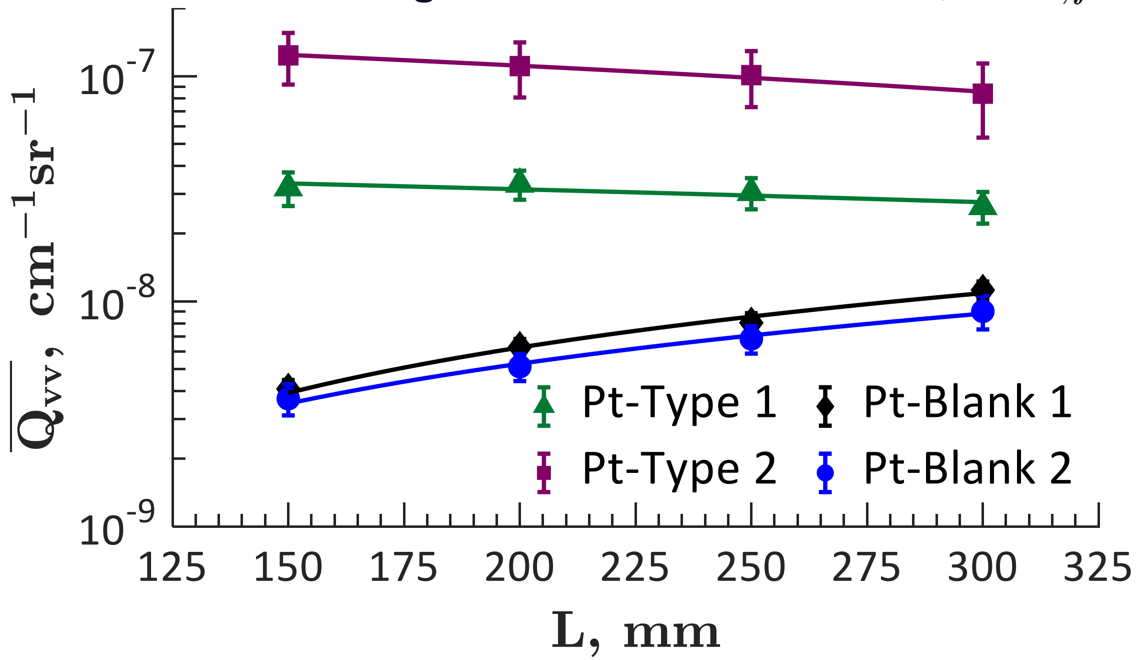
$Q_{vv,Pt}$:scattering coefficient of the Pt flame

$Q_{vv,Blank}$:scattering coefficient of the Blank flame

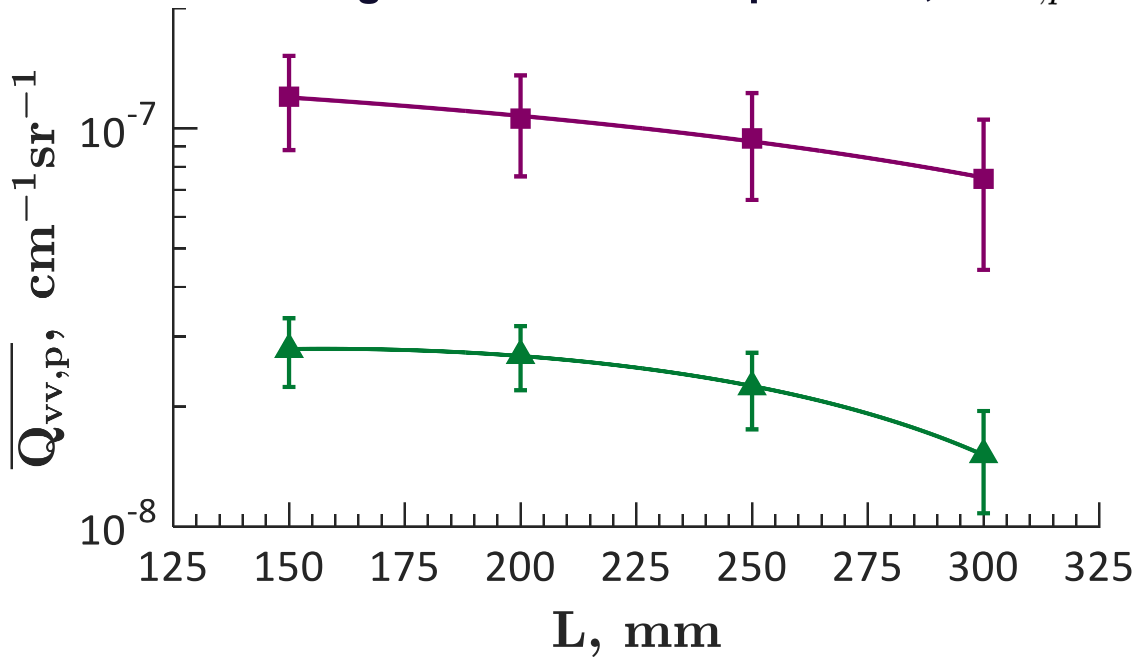
$$Q_{vv,p} = Q_{vv,Pt} - Q_{vv,Blank}$$

$Q_{vv,p}$:scattering coefficient of the particles

Scattering coefficient of the flames, $Q_{vv,f}$



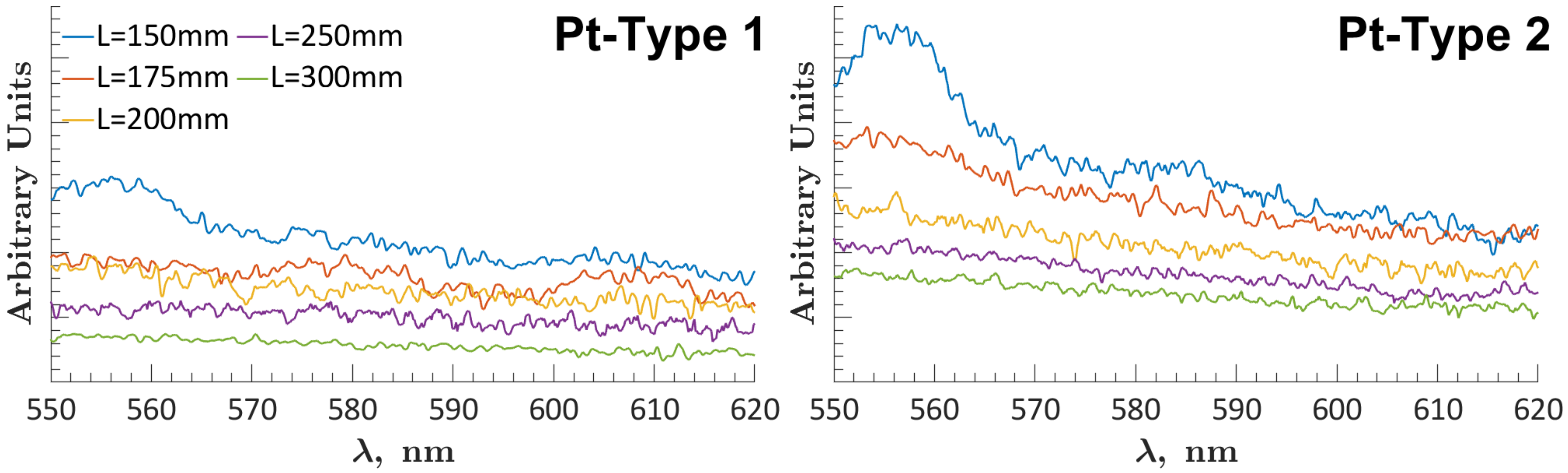
Scattering coefficient of the particles, $Q_{vv,p}$



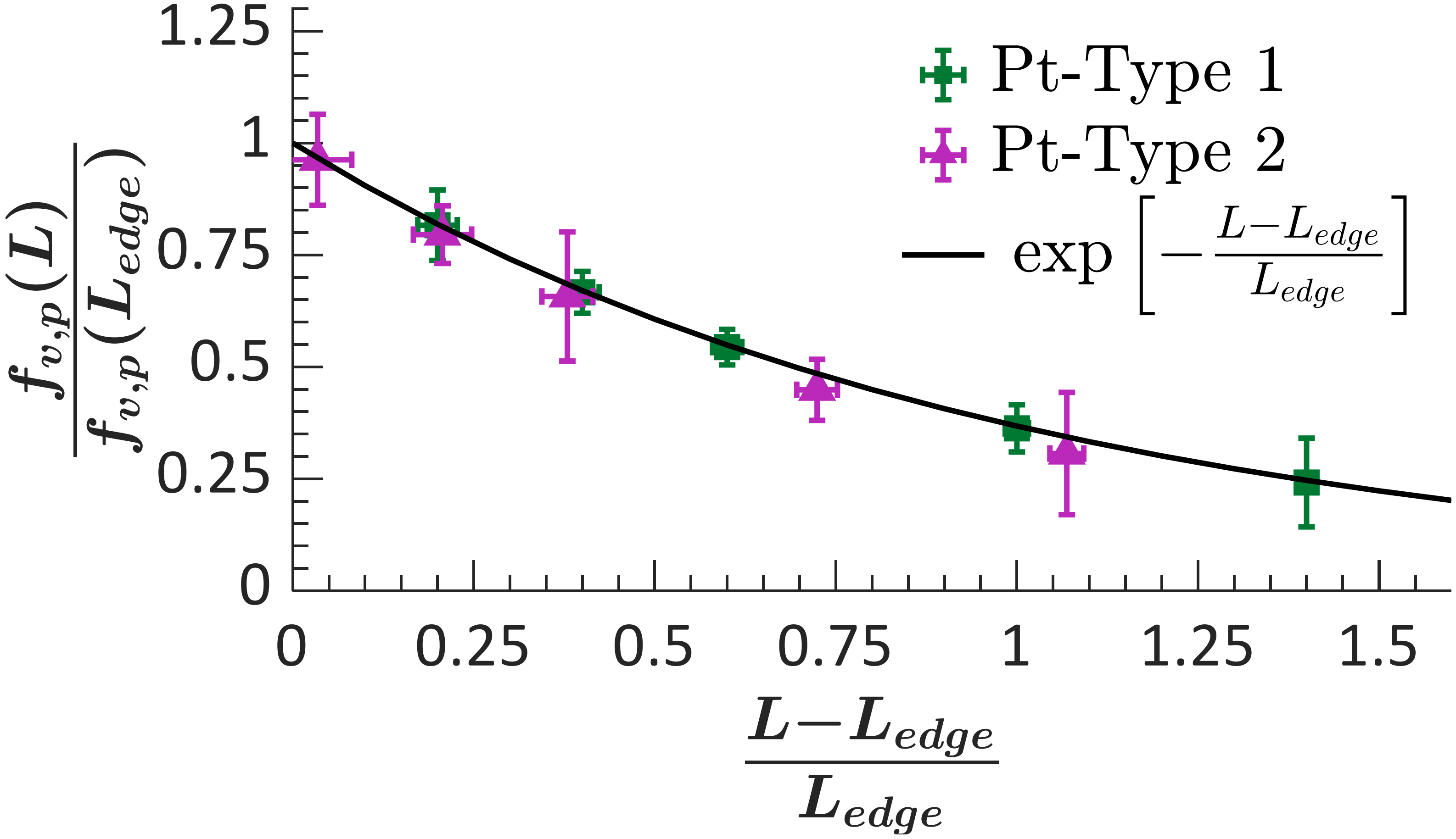
- ❑ **Decrease of the scattering coefficient as the nanoparticles are convected downstream of the flame due to dilution in the surrounding gases**

Laser Induced Incandescence

LII signal comparison



- ❑ **LII spectral emission decreases at increasing distance from the fuel nozzle, L**
- ❑ **Nanoparticle vaporization temperature achieved by laser heating (e.g., ~5200 K at L=150mm in Pt-type2) increases at increasing L**



$$f_{v,p}(L) = \frac{\overline{S_{LII}}(L)}{\overline{S_{LII}}(L_{edge})} f_{v,p}(L_{edge})$$

- **Pure Pt assumption:**

$$f_{v,p_{Pt}}(L_{edge}) = 8.70 \cdot 10^{-8}$$

- **Pure PtO_2 assumption :**

$$f_{v,p_{PtO_2}}(L_{edge}) = 2.14 \cdot 10^{-7}$$

- **We introduce an equation to estimate the volume fraction that predicts the results of LII measurements. The exponential law is typical of (turbulent) diffusion mixing**

In-situ Laser Diagnostics

Particle size

$$\overline{d_{6,3}} = \left(\frac{\overline{d^6}}{\overline{d^3}}\right)^{\frac{1}{3}} = \left(\frac{Q_{vv,p}}{\frac{6}{\pi}\cdot f_{v,p}\cdot\frac{\pi^2}{4\lambda^4}\cdot F(m)}\right)^{\frac{1}{3}}$$

λ : **wavelength of the used laser**

m : **complex refractive index**

$F(m)$: **scattering function**

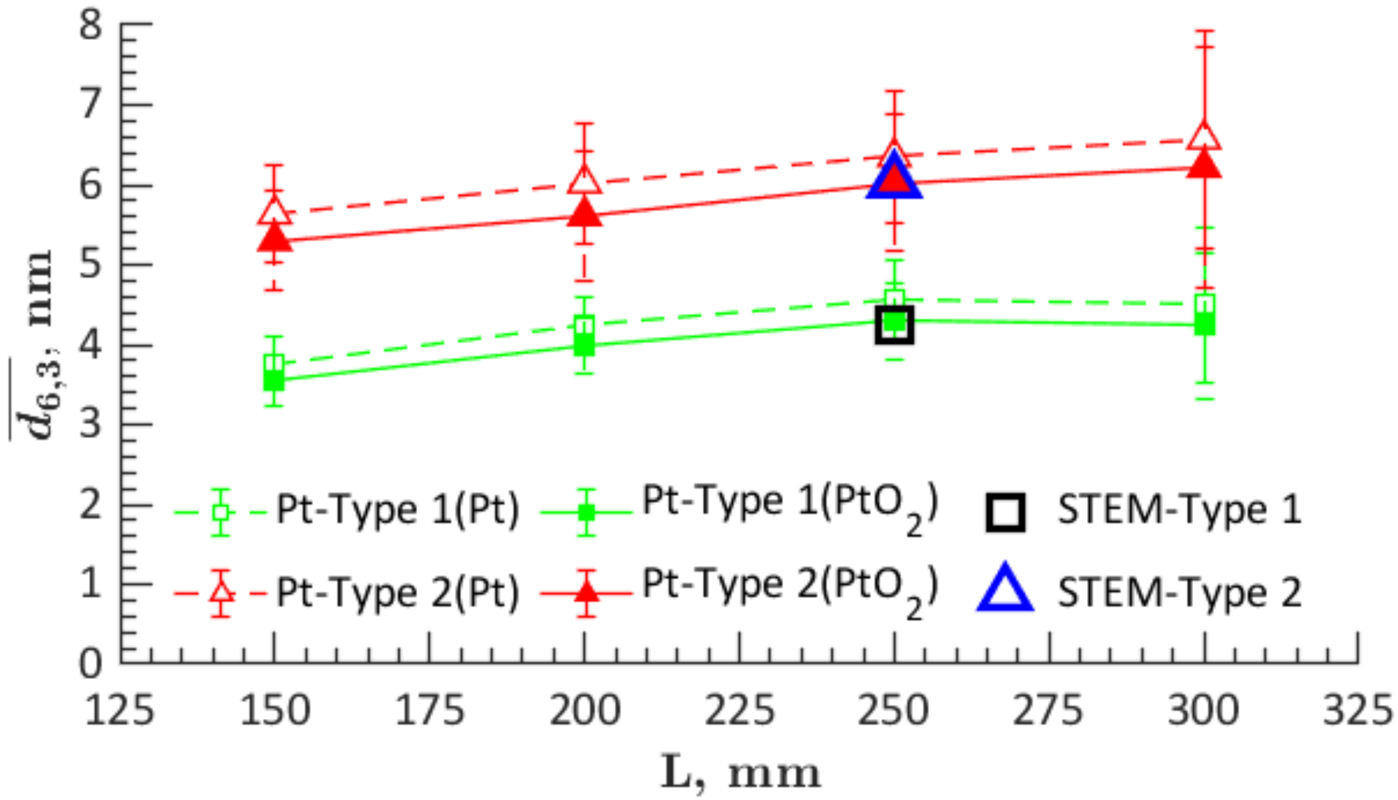
$$F(m) = \left|\frac{m^2-1}{m^2+2}\right|^2$$

For Pt: $F(m_{Pt}) = 1.23 \pm 0.06$

$$f_{v,p_{Pt}}\ (L_{edge}) = 8.70\cdot 10^{-8}$$

For PtO_2: $F(m_{PtO_2}) = 0.60 \pm 0.03$

$$f_{v,p_{PtO_2}}\ (L_{edge}) = 2.14\cdot 10^{-7}$$



- **The LS equivalent diameter of Pt-Type 2 is larger than the one of Pt-Type 1**
- **The results are consistent regardless of the assumption on the oxidation degree of the synthesized particles**
- **The LS equivalent diameter is consistent with the HAADF-STEM image analysis in both cases (Pt-Type 1 and Pt-type 2)**

Ex-situ Particle Size Distribution (PSD)

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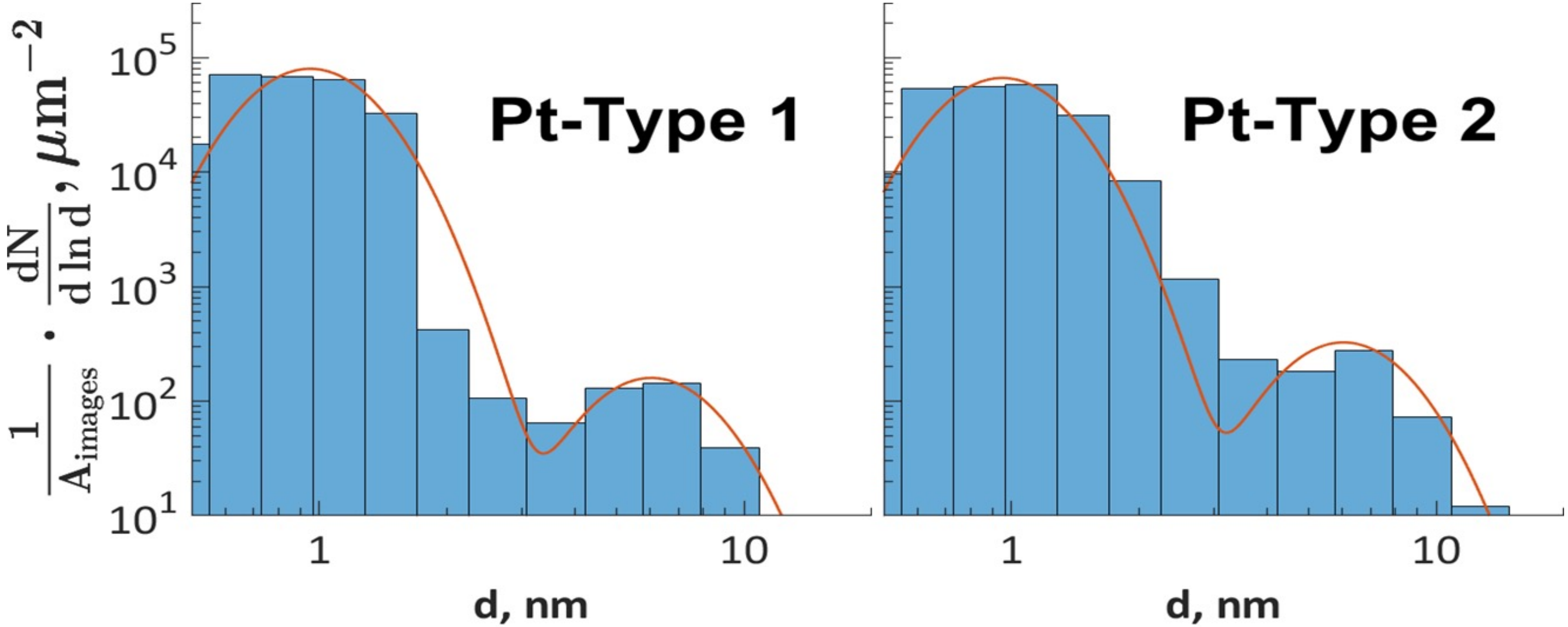
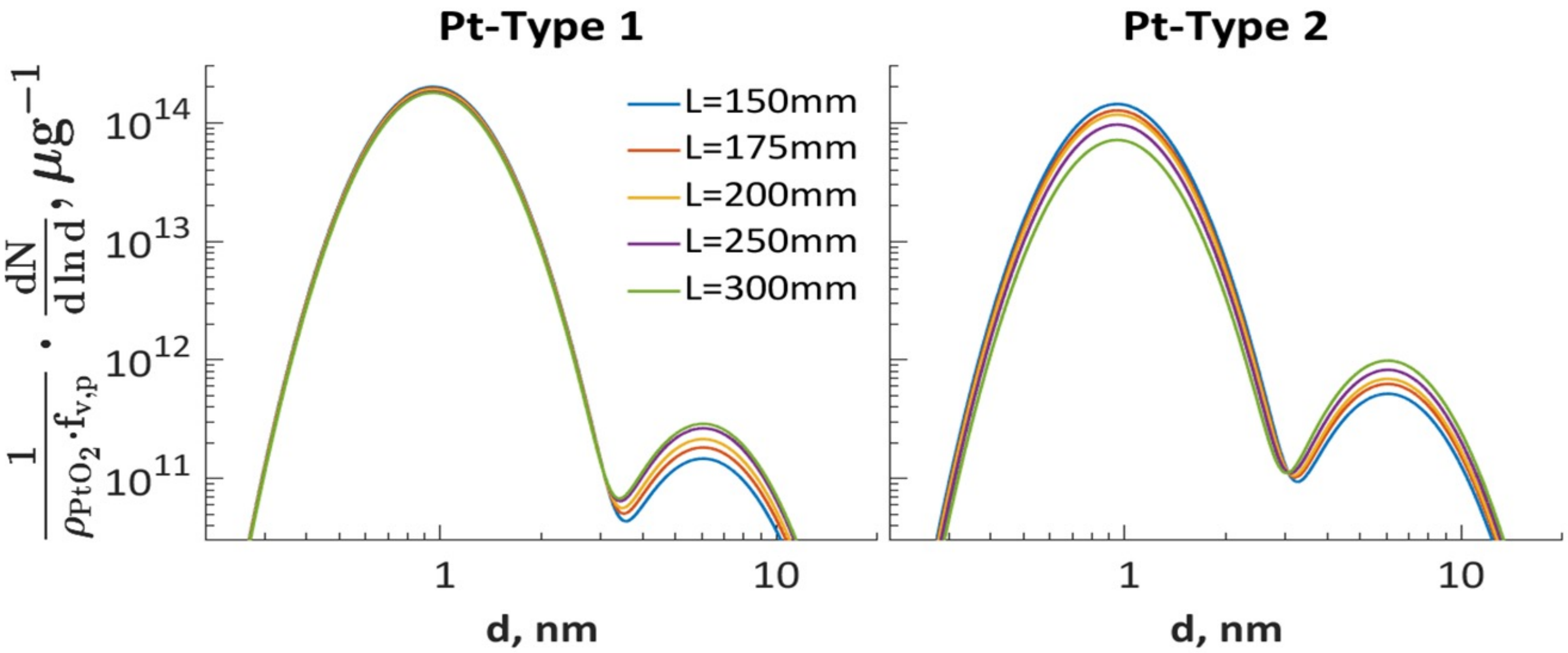
Bimodal distribution



- Bimodal distribution with first and second mode median diameter positioned at 0.95nm and 6.05nm regardless of the Pt flame type
- Number concentration of the second mode in the Pt-Type 2 flame is larger than in Pt-Type 1 resulting in larger $d_{6,3}$ measured via LS
- The sum of the same two log-normal fits microscopy results in both flames

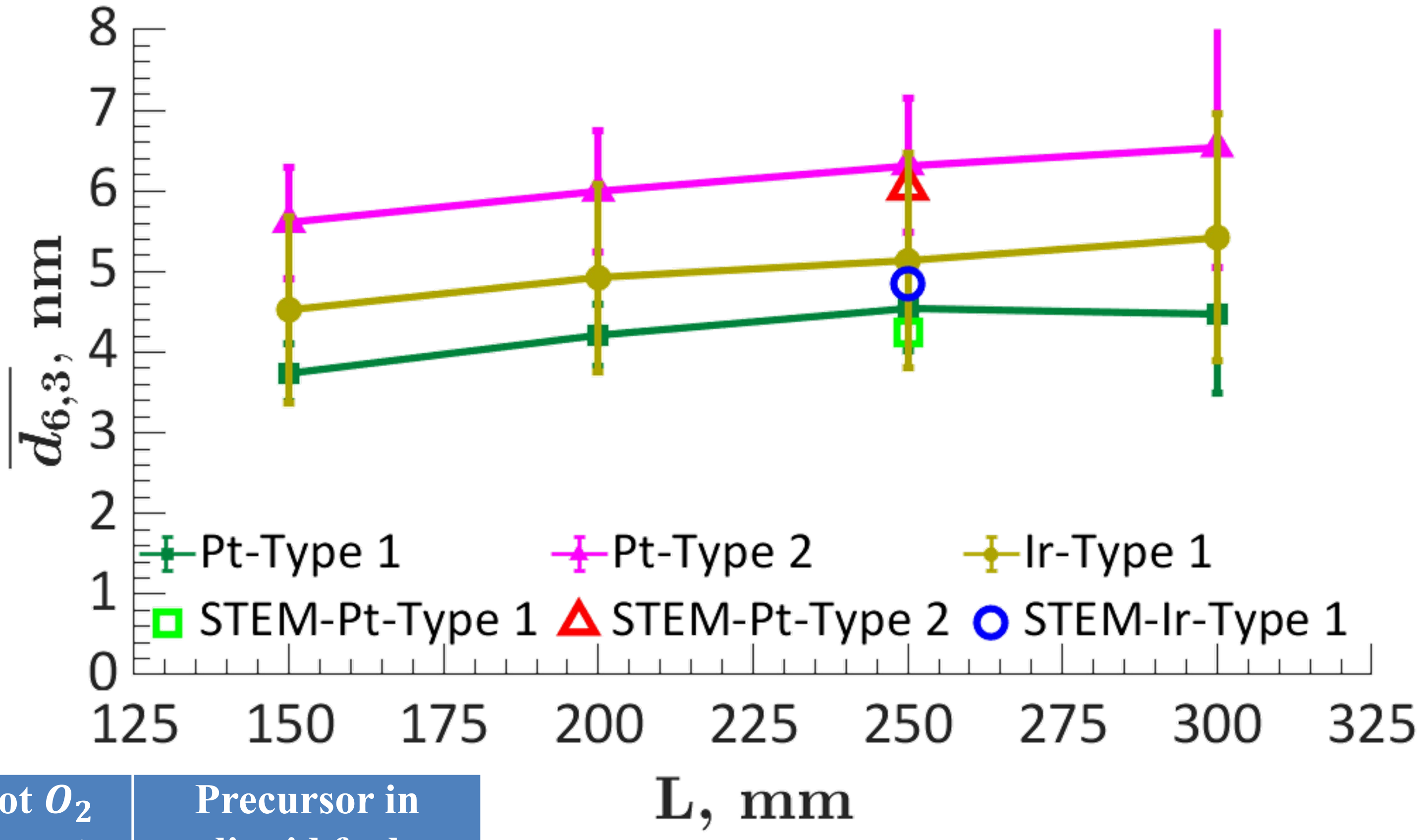
Particle Size Distribution

PSDs per unit total mass



- **Same modes are inferred at all Ls from the $d_{6,3}$ measured by LS**
- **The number of particles in the second mode increases as the nanoparticles are convected downstream of the flame resulting in the slight increase of $d_{6,3}$**
- **Number concentration of the second mode in the Pt-Type 2 flame is larger than in Pt-Type 1 throughout the flames**
- **The synthesized nanoparticles appear to grow at rates that are orders of magnitude slower than the collision rate of non-interacting Brownian nanoparticles**

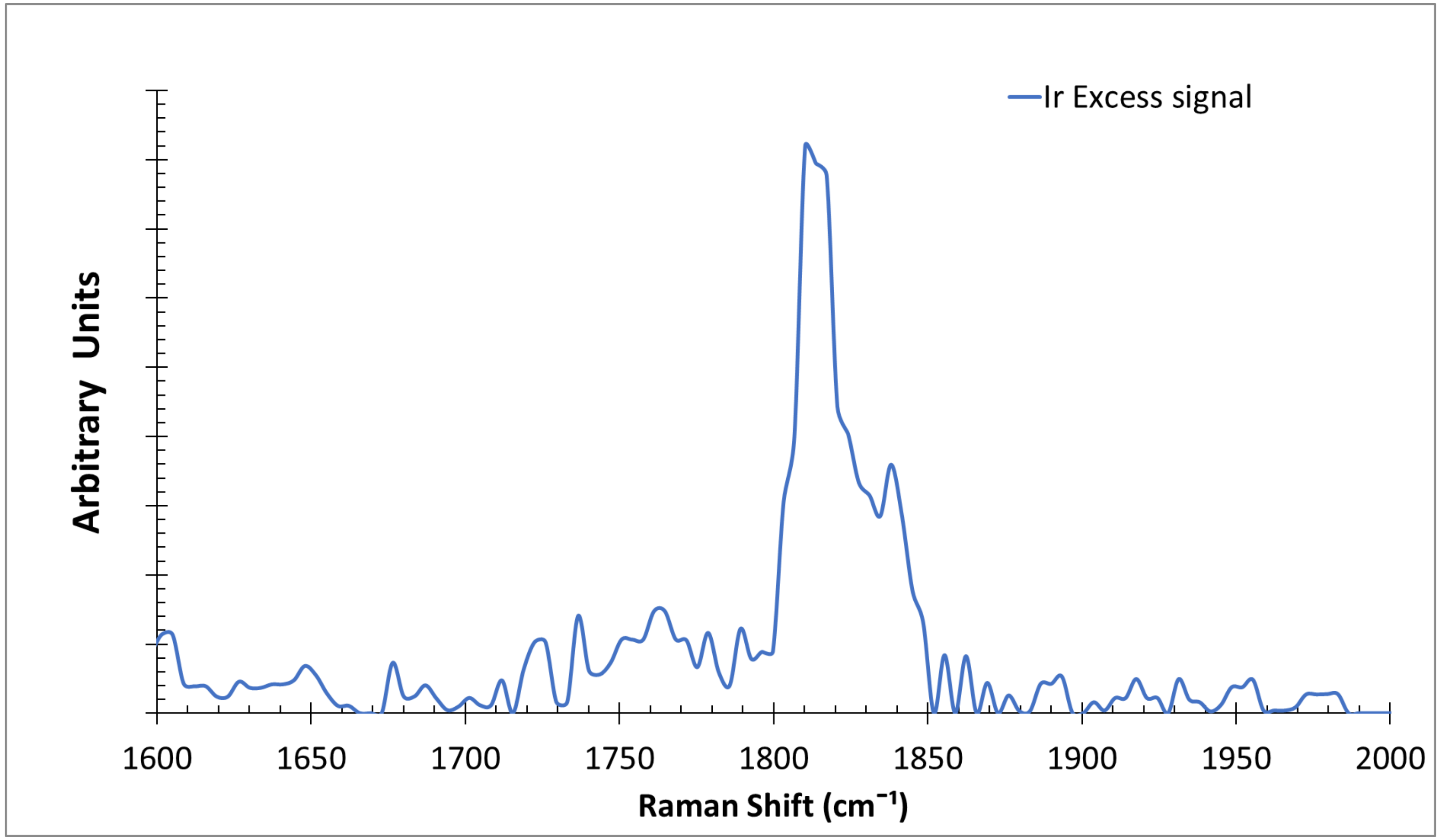
- The LS equivalent diameter of Ir-Type1 lies between LS equivalent diameter of Pt-Type1 and Pt-Type2
- The LS equivalent diameter of Ir-Type1 is consistent with the HAADF-STEM image analysis of the samples



Flame name	Liquid fuel mixture (mL/min)	O_2 (SLPM)	Pilot CH_4 flow rate (SLPM)	Pilot O_2 flow rate (SLPM)	Precursor in liquid fuel
Pt-Type 1	4	7.3	0.55	0.55	10 mM PtAcAc
Pt-Blank 1	4	7.3	0.55	0.55	-
Pt-Type 2	7	11	0.75	0.75	10mM PtAcAc
Pt-Blank 2	7	11	0.75	0.75	-
Ir-Type 1	8	12	0.75	0.75	9mM IrAcAc
Ir-Blank 1	8	12	0.75	0.75	-

Current Work

Raman measurements in Ir nanoparticles



- **A Raman peak is detected in the Ir flame at ~1820 cm^{-1} which is not present in the blank flame.**
- **Preliminary investigation suggests that the peak is, due to the presence of carbonyl groups on the surface of the synthesized nanoparticles**

Conclusions

- **Identified a simple methodology for rapidly predicting the axial profile of the nanoparticle volume fraction downstream of two RSDT flames**
- **Pt nanoparticles withstand progressively higher vaporization temperatures as they are aging in the flame, possibly due to changes in their phase and/or degree of oxidation**
- **The PSDs are composed of two lognormal modes centered at approximately 1 nm and 6 nm, with the relative number of nanoparticles belonging to the larger mode being determined by the RSDT flame operating parameters for the investigated precursor solution**
- **The synthesized nanoparticles appear to grow at rates that are orders of magnitude slower than the collision rate of non-interacting Brownian nanoparticles**
- **Preliminary Raman results of Ir flame suggest the attachment of carbonyl groups on the surface of the synthesized nanoparticles**

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Questions

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